

METHOD OF MANUFACTURING FERROELECTRIC SUBSTANCE
THIN FILM AND FERROELECTRIC MEMORY USING
THE FERROELECTRIC SUBSTANCE THIN FILM

5 Background of the Invention

The present invention relates to a method of manufacturing a ferroelectric substance thin film and a method of manufacturing a ferroelectric memory, particularly to improvement of crystallinity of the ferroelectric substance thin film.

10 The ferroelectric memory being researched now is divided into two. One is a system detecting reverse charge quantity of a ferroelectric capacitor constructed with the ferroelectric capacitor and a selective transistor.

Another one is a memory of a system detecting change of
15 resistance of a semiconductor caused by spontaneous polarization of the ferroelectric substance. The typical one of the system is MFSFET. This is an MIS structure using the ferroelectric substance for a gate insulating film.

In any structure, it is known that film quality of the
20 ferroelectric substance affects to characteristics of memory largely.

Then, various methods improving crystallinity of the ferroelectric thin film are proposed. As one of them, a method of crystallization of a PZT thin film called Ti seed method
25 is proposed.

As shown in Fig. 7, the method includes forming a seed layer 9L consisting of titanium ultra thin film of about 20 nm film thickness on surface of a lower electrode 8 consisting of platinum Pt and the like by sputtering method and to form
5 a PZT film 9P on the upper layer by sol-gel method as shown in Fig. 7. Here, mixed solution of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$, and $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ is used as a starting material, after spin-coating the mixed solution, is dried at 150°C , and temporary baking of 400°C , 30 minutes is performed at dry air
10 atmosphere. After repeating this five times, crystal growth from the ultra thin film 9L appears through crystallization annealing process of about 700°C , one minute in atmosphere of O_2 .

In the method, there has been a problem that particle
15 diameter of crystal can not be controlled because a place where crystallization starts is unstable and dispersion of characteristic is large because uniform size columnar crystal is formed so as not to obtain enough characteristics particularly at micronization and high integration.

20 There has been a problem that the method has a place becoming titanium oxide layer (TiO_2) or lead titanate (PbTiO_3) layer without becoming PZT film so as to obtain good characteristics.

There has been a problem that the method affects badly
25 to substrate layer such as substrate wiring because temperature

at crystallization annealing was high temperature about 700°C.

Summary of the Invention

The invention is performed in view of the circumstances,
5 and an object of the invention is to provide a ferroelectric
thin film uniform and good in crystallinity.

The invention is characterized by forming a seed layer
including ultra-fine particle powder including composing
element of a ferroelectric substance thin film on a surface
10 of a substrate constructing the substrate before forming the
ferroelectric substance thin film and forming the ferroelectric
substance thin film on an upper layer of the seed layer so as
to performing crystallization making the seed layer a nucleus.

According to such the construction, it is possible to
15 obtain a ferroelectric substance thin film uniform and good
in crystallinity because crystallization advances well making
the ultra-fine particle powder a nucleus by existence of the
ultra-fine particle powder. It is desirable to make the
ultra-fine particle powder from 0.5 nm to about 200 nm particle
20 diameter, particularly from 1 nm to about 50 nm particle
diameter.

Incidentally, some degree of number of atoms is need for
the ultra-fine particle powder to become a nucleus, the
ultra-fine particle powder can not become the nucleus with one
25 atom, and it is desirable to be larger size enough than atomic

of about 0.1 nm. On the other hand, when the nucleus is too large, center of the nucleus remains as Ti. Therefore, high annealing temperature is need for not remaining Ti. It is impossible to form a flat and uniform ferroelectric substance thin film when the size is larger than 200 nm. There is inconvenience that the nucleus is hard to scatter in solution when the nucleus is large.

Further, the concentration is desirable to be from 0.00001 wt% (0.1 wtppm) to about 1 wt%.

Desirably, the invention is characterized by including a process forming a seed layer including titanium ultra-fine particle powder becoming a seed and a process forming a PZT thin film on the upper layer of the seed layer.

According such the construction, it is possible to obtain a PZT ferroelectric substance thin film uniform and good in crystallinity because crystallization advances well making the titanium ultra-fine particle powder a nucleus by existence of the titanium ultra-fine particle powder of about 5 nm diameter.

Desirably, the invention is characterized by that the process forming the seed layer includes a process applying solution including the titanium ultra-fine particle powder and a process drying and baking.

According such the construction, it is possible to arrange the titanium ultra-fine particle powder easily and uniformly.

Desirably, the invention is characterized by that the

process forming the PZT thin film includes a sputtering process.

Desirably, the invention is characterized by that the process forming the PZT thin film further includes an annealing process for crystallization.

5 According such the construction, it is possible to form easily a good ferroelectric substance thin film in crystallinity by introducing an annealing process for crystallization though it is possible to perform crystallization at a heating process in the following forming process or forming an electrode an
10 insulating film too because crystal growth at about 450°C, lower temperature than the related art.

 The second method of the invention is characterized by including a process applying a ferroelectric substance thin film applying liquid including ultra-fine particle powder
15 including at least one kind of composing elements of the ferroelectric substance thin film on a surface of a substrate constructing a substrate and a baking process.

 According to such the construction, crystallization from the ultra-fine particle powder advances well because of forming
20 thin film including ultra-fine particle powder and it is possible to form a thin film uniform and high in reliability.

 Desirably, the invention is characterized by including a process applying a PZT applying liquid including ultra-fine particle powder becoming a seed on a surface of a substrate.
25 constructing a substrate and a baking process.

According to such the construction, crystal growth starts from a seed consisting of titanium ultra-fine particle powder of about 5 nm particle diameter scattered uniformly in whole of the ferroelectric substance thin film. Therefore, it is possible to form the PZT ferroelectric substance thin film uniform and good in crystallinity because crystallization advances well making the titanium particle powder a nucleus.

Desirably, the invention is characterized by further including an annealing process for crystallization.

According such the construction, it is possible to form easily a good ferroelectric substance thin film in crystallinity by introducing an annealing process for crystallization though it is possible to perform crystallization at a heating process in the following forming process or forming an electrode an insulating film too because crystal growth at about 450°C, lower temperature than the related art.

The third invention is characterized in that forming the ferroelectric substance film is performed by forming a seed layer including an ultra-fine particle powder including composing element of the ferroelectric substance thin film on surface of a floating gate before forming the ferroelectric substance thin film and by carrying out crystal growth making the ultra-fine particle powder a nucleus at a method of manufacturing a ferroelectric substance consisting of an FET of an MFMIS structure.

According to such the construction, it is possible to obtain a ferroelectric substance thin film uniform and good in crystallinity because crystallization advances well making the ultra-fine particle powder a nucleus by existence of the
5 ultra-fine particle powder of about 5 nm diameter so that it is possible to form high ferroelectric substance memory in reliability.

In the fourth invention, forming process of the ferroelectric substance film is performed by applying a
10 ferroelectric substance thin film applying liquid including an ultra-fine particle powder including at least one kind of composing elements of the ferroelectric substance thin film on a surface of a substrate constructing a substrate and forming the ferroelectric substance thin film so as to make it
15 crystallization in a method of manufacturing a ferroelectric substance memory consisting of an FET of an MFMIS structure.

According to such the construction, a uniform ferroelectric substance thin film is obtained because crystal growth starts from a seed scattered uniformly in whole
20 ferroelectric substance thin film, and it is possible to form high ferroelectric substance memory in reliability at michronization.

The fifth invention is characterized in that a ferroelectric substance thin film of the ferroelectric
25 substance capacitor is formed by applying a ferroelectric

substance thin film applying liquid including ultra-fine
particle powder including at least one kind of composing elements
of the ferroelectric substance thin film on a surface of a first
electrode and making it crystallization in a method of
5 manufacturing a ferroelectric substance memory consisting of
a switching transistor and a ferroelectric capacitor.

According to such the construction, a uniform
ferroelectric substance thin film is obtained because crystal
growth starts from a seed scattered uniformly in whole
10 ferroelectric substance thin film, and it is possible to form
high ferroelectric substance memory in reliability at
micronization.

The sixth invention is characterized in that a
ferroelectric substance thin film of the ferroelectric
15 substance capacitor is formed by forming a strong seed layer
including ultra-fine particle powder including at least one
kind of composing elements of the ferroelectric substance thin
film on a surface of a first electrode, forming the ferroelectric
substance thin film on an upper layer of the seed layer, and
20 forming the ferroelectric substance thin film consisting of
crystals being all of a size making it crystallization in a
method of manufacturing a ferroelectric substance memory
consisting of a switching transistor and a ferroelectric
capacitor.

25 According such the construction, it is possible to obtain

a ferroelectric substance thin film uniform and good in crystallinity because crystallization advances well making the ultra-fine particle powder a nucleus and to form high ferroelectric substance memory in reliability by existence of
5 the titanium ultra-fine particle powder of about 5 nm diameter.

Brief Description of the Drawings

Fig. 1 is a view showing an FRAM using an insulating film formed by a method of a first embodiment of the invention;

10 Figs. 2A to 2E are views showing a manufacturing process of the FRAM of Fig. 1;

Fig. 3 is a describing view of the principle describing a method of the first embodiment of the invention;

15 Fig. 4 is a describing view showing an FRAM formed by a method of a second embodiment of the invention;

Figs. 5A to 5E are views showing a manufacturing process of the FRAM of Fig. 4;

Fig. 6 is a describing view of the principle describing a method of the second embodiment of the invention; and

20 Fig. 7 is a describing view of the principle describing a method of the related art.

Detailed Description of the Preferred Embodiment

An embodiment of a ferroelectric substance memory and
25 a method of manufacturing the same according to the invention

will be described referring drawings.

(Embodiment 1)

A ferroelectric substance memory using a ferroelectric substance capacitor using a PZT as a ferroelectric substance film will be described for a first embodiment of the invention. A completing view of the ferroelectric substance memory is shown in Fig. 1 and manufacturing process views are shown in Figs. 2A to 2E. The ferroelectric substance memory relates to a ferroelectric substance memory (FRAM) forming a ferroelectric substance capacitor on an insulating film 6 covering a surface of a substrate so as to connect one side of source-drain regions 2 and 3 of an MOSFET functioning as a switching transistor formed in a silicon substrate 1 and lower electrodes 8a and 8b through plugs 7, and crystallinity of a ferroelectric substance thin film 9 of the ferroelectric substance capacitor is uniform. Here, symbol 5 is a gate electrode formed on surface of the substrate through a gate insulating film 4. The ferroelectric substance thin film 9 includes a crystal having uniform particle diameter of crystal formed so as to make crystal growth generate from the titanium ultra-fine particle powder by previously forming a seed layer including titanium ultra-fine particle powder on surface of the lower electrode.

That is, as shown in Fig.1, the plugs 7 of polycrystalline silicon layer doped in high density is formed, the lower electrodes 8 of two layers film of iridium 8a and iridium oxide

8b is formed, and a ferroelectric substance thin film 9 in uniform crystalline (See Fig. 3) on the lower electrodes 8 by crystal growth making a seed layer S of titanium ultra-fine particle powder a nucleus and further forming upper electrodes 10 of two layers film of iridium oxide and iridium on the upper layer of the ferroelectric substance thin film.

Next, a process for manufacturing the ferroelectric substance memory will be described with reference to Figs. 2A to 2E.

First, thermal oxidation is performed about the surface of the silicon substrate 1 forming a MOSFET (not shown) in an element region formed with an element separating insulating film 1S formed by LOCOS method, and after forming the insulating film 6 of silicon oxide of about 600 nm film thickness, a contact hole H is formed at the insulating film 6. After a polycrystal silicon layer doped in high density in the contact hole so as to form the plug 7, the iridium layer 8a of about 200 nm film thickness is formed at whole surface of the substrate by sputtering method and further the surface thereof is oxidized so as to become iridium oxide 8b as shown in Fig. 2A.

Continuously, the iridium oxide layer is patterned to photolithography so as to form the lower electrode 8.

After that, Ti ultra-fine particle powder of about 5 nm particle diameter is mixed with a surface active agent of 0.1 to 10 wt% and α terpineol and the mixed liquid is applied as

shown in Fig. 2B.

After that, a PZT film 9P for forming the ferroelectric substance film 9 is formed as shown in Fig. 2C. Mixed solution of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$, and $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ is used as a starting material. After spin coating the mixed solution, the film is dried at 150°C , and temporary baking of 400°C , 30 minutes is performed at dry air atmosphere. This is repeated five times. After that, thermal treatment of about 450°C , one minute in atmosphere of O_2 is performed as shown in Fig. 2D.

Thus, a ferroelectric substance film 10 of 250 nm is formed as shown in Fig. 2E. Here, the PZT film is formed placing 0.52 for x (PZT (52/48) hereafter) in $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$.

A laminating layers film of iridium oxide and iridium is formed on the ferroelectric substance film 9 by sputtering. The laminating layers film of iridium oxide layer and iridium layer form an upper electrode 10. Here, the iridium layer and the iridium oxide layer are formed so as to be 200 nm thickness in all. Thus, the ferroelectric substance capacitor is obtained.

According to such the structure, it is possible to obtain a ferroelectric substance thin film uniform and good in crystallinity because crystallization advances well making the ultra-fine particle powder a nucleus by existence of the ultra-fine particle powder as shown in Fig. 3.

It is desirable that the ultra-fine particle powder has

from 0.5 nm to about 200 nm particle diameter, particularly from 1 nm to about 50 nm particle diameter.

Incidentally, some degree of number of atoms is need for the ultra-fine particle powder to become a nucleus, the
5 ultra-fine particle powder can not become the nucleus with one atom, and it is desirable to be larger size enough than atomic of about 0.1 nm. On the other hand, when the nucleus is too large, center of the nucleus remains as Ti. Therefore, high annealing temperature is need for not remaining Ti. It is
10 impossible to form a flat and uniform ferroelectric substance thin film when the size is larger than 200 nm. There is inconvenience that the nucleus is hard to scatter in solution when the nucleus is large.

Further, the concentration is desirable to be from 0.00001
15 wt% (0.1 wtppm) to about 1 wt%. Although a substance that the circumference of Ti ultra-fine particle powder is covered with surface active agent and organic solvent such as α terpineol is mixed for forming the seed layer, it is possible too to use xylene, toluene, 2-methoxyethanol, butanol and so on as organic
20 solvent.

Desirably, at the process forming the seed layer, solution including the titanium ultra-fine particle powder is applied, and after that, drying and baking are performed.

According to such the construction, it is possible to
25 arrange the titanium ultra-fine particle powder easily and

uniformly.

The process forming the PZT thin film may be by sputtering method except sol-gel method.

Desirably, the process forming the PZT thin film further
5 includes an annealing process for crystallization.

According such the construction, it is possible to form easily a good ferroelectric substance thin film in crystallinity by introducing an annealing process for crystallization though it is possible to perform crystallization at a heating process
10 in the following forming process or forming an electrode an insulating film too because crystal growth at about 450°C, lower temperature than the related art.

Although the ferroelectric substance memory using PZT as the ferroelectric substance thin film is described for the
15 first embodiment of the invention, it is not need to say that another material such as the ferroelectric substance memory using STN as the ferroelectric substance film may be applicable.

(Embodiment 2)

Next, a manufacturing process of a ferroelectric
20 substance memory of the MFMIS structure will be described. Fig. 4 is a view showing the ferroelectric substance memory formed by the method of the invention, and Figs. 5A to 5E are views manufacturing process.

In this example, a ferroelectric substance thin film
25 of the ferroelectric substance memory of the MFMIS structure

is formed by applying sol-gel liquid including Ti ultra-fine particle powder, and after baking, by crystallization-annealing so as to form the ferroelectric substance thin film 16 uniform and high in crystallinity.

5 That is, the ferroelectric substance memory is constructed by source-drain regions 2 and 3 formed on surface of a silicon substrate 1, a floating gate 15 formed between them through a gate insulating film 4, a ferroelectric substance thin film 16 formed on the floating gate 15, and a control gate
10 17 formed on the ferroelectric substance thin film 16.

At manufacturing, as shown in Fig. 5A, after surface of n-type silicon substrate 1 is oxidized thermally so as to form a silicon oxide layer 4 of about 20 nm film thickness, an iridium layer becoming the floating gate 15 is formed on the silicon
15 oxide layer 4 using iridium as a target by sputtering method. Next, performing thermal treatment of 800°C, one minute in atmosphere of O₂ so as to form an iridium oxide layer on surface of the iridium layer.

Next, a PZT film is formed on the floating gate 15 as
20 the ferroelectric substance film 16 by sol-gel method as shown in Fig. 5B. Titanium ultra-fine particle of 5 nm particle diameter of 0.5 wt%, surface active agent of 1 wt%, and mixed solution of Pb(CH₃COO)₂·3H₂O, Zr(t-OC₄H₉)₄, and Ti(i-OC₃H₇)₄ are used as starting materials. After spin coating the mixed
25 solution, the film is dried at 150°C, and temporary baking of

400°C, 30 minutes is performed at dry air atmosphere. After this is repeated five times, thermal treatment of 500°C, one minute in atmosphere of O₂ is performed as shown in Fig. 5C. Thus, a ferroelectric substance film 16 of 250 nm is formed.

5 Here, the PZT film is formed placing 0.52 for x in PbZr_xTi_{1-x}O₃ (PZT(52/48), hereinafter).

Here, a uniform ferroelectric substance thin film can be obtained because crystal growth starts from the seeds scattered uniformly in whole of the ferroelectric substance thin film so as to form high ferroelectric substance thin film in reliability at micronization.

Further, an iridium layer and an iridium oxide layer are formed on the ferroelectric substance film 16 by sputtering so as to form a control gate 17. Here, the iridium layer and the iridium oxide layer are formed so as to be 200 nm thickness in all.

Then, a resist pattern R is formed on the upper layer thereof and each layer is patterned masking the pattern as shown in Fig. 5D so as to expose surfaces of regions becoming source-drain.

After that, by injecting boron (B) ion masking the gate electrode pattern, source-drain regions 2 and 3 of p-type diffusion layer as shown in Fig. 5E.

Further, forming a layer insulating film and a wiring pattern, a ferroelectric substance memory is completed.

According to such the structure, since the ferroelectric substance film formed between the floating gate and the control gate is a film uniform and good in crystallinity, the memory has high reliability without having dispersion of characteristics.

Although PZT is used for the ferroelectric substance film, the ferroelectric substance such as STN, SBT and the like or the high permittivity dielectric film such as BST and the like are possible to apply. Material included in composing element of the ferroelectric substance film may be applied for ultra-fine particle powder.

As described above, the invention forms a seed layer including ultra grain particle containing element constituting a ferroelectric substance thin film on a surface of a substrate constructing the substrate before forming the ferroelectric substance thin film and forms the ferroelectric substance thin film on an upper layer of the seed layer so as to perform crystallization making the seed layer a nucleus. Therefore, it is possible to obtain a ferroelectric substance thin film uniform and good in crystallinity because crystallization advances well making the ultra-fine particle powder a nucleus by existence of the ultra-fine particle powder.

The method of the invention applies a ferroelectric substance thin film applying liquid including ultra-fine particle powder containing at least one kind of elements

constituting the ferroelectric substance thin film on a surface of a substrate constructing a substrate and forms a thin film including ultra-fine particle powder. Therefore, crystallization advances well from the ultra-fine particle powder because of forming thin film including ultra-fine particle powder scattering in whole of thin film and it is possible to form a thin film uniform and high in reliability.